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# (54) Ink compositions for ink-jet recording

(57) The invention relates to ink compositions for ink-jet recording which can avoid clogging of nozzles. An ink composition for ink-jet recording comprising a

pigment and a compound containing 5 to 90 moles of ethylene oxide per 1 mole of polyglycerin having a polymerization degree of 2 to 10, optionally in an aqueous medium, is provided.

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The polymerization degree of said polyglycerin is preferably in the range of about 2 to 10.

The compound wherein ethylene oxide is added to polyglycerin may be used in an amount of 0.5 to 30% by weight, preferably 2 to 20% by weight, more preferably 3 to 15% by weight on the basis of the total weight of the ink composition for ink-jet recording. If the amount is less than 0.5% by weight, clogging of nozzles can not be prevented and therefore the ejection responsivity can not be maintained. If the amount is more than 30% by weight, the ink viscosity may increase unnecessarily or the fluidity may be lowered.

The pigment used in ink compositions for ink-jet recording according to this invention may be any of known inorganic or organic pigments which are dispersible in an aqueous medium, and especially preferred are those readily wettable in an aqueous medium by surface treatment.

Inorganic pigments which may be used include titanium dioxide, red iron oxide, antimony red, cadmium red, cadmium yellow, cobalt blue, Prussian blue, ultramarine blue, carbon black, graphites, etc., and organic pigments include soluble azo pigments, insoluble azo pigments, azo lake pigments, condensed azo pigments, copper phthalocyanine pigments, condensed polycyclic pigments, etc.

The pigment may be used in an amount of 1 to 30% by weight, preferably 2 to 10% by weight on the basis of the total weight of the ink composition for ink-jet recording. If the amount is too small, the color concentration will be lowered. If the amount is too large, however, the ink viscosity will increase or the fluidity will be lowered.

The aqueous medium used in ink compositions for ink-jet recording according to this invention may be water or water-miscible solvents which have been commonly used in the technical field to which this invention belongs.

Water-miscible solvents include lower alcohols, polyhydric alcohols and their derivatives, nitrogen-containing cyclic compounds, etc.

Specific examples are lower alcohols such as methanol, ethanol, normal propanol, isopropanol; polyhydric alcohols such as ethylene glycol, propylene glycol, diethylene glycol, dipropylene glycol, glycerin; polyhydric alcohol derivatives such as ethylene glycol monomethyl ether, ethylene glycol monoethyl ether, propylene glycol monomethyl ether, propylene glycol monomethyl ether, dipropylene glycol monomethyl ether, dipropylene glycol monomethyl ether, dipropylene glycol monomethyl ether, nitrogen-containing cyclic compounds such as N-methylpyrrolidone, N-ethylpyrrolidone, etc.

Water-miscible solvents such as acetone or ethyl acetate are not preferable because they may damage printers. If the resulting printed matters should have high fixability and water fastness or if the ink composition for ink-jet recording should have a high pigment-dispersibility, the ink composition for ink-jet recording may also include an aqueous resin or a basic compound used for dissolving or dispersing the aqueous resin into an aqueous medium, if desired.

The aqueous resin may be such as is commonly used in the technical field to which this invention belongs.

Specific examples include the aqueous resins mentioned in Japanese Patent Application No. 255223/95 filed by the present applicant, acrylic alkyl ester-(meth)acrylic acid copolymers, styrene-acrylic acid copolymers, styrene-acrylic acid-acrylic alkyl ester copolymers, styrene-maleic acid-acrylic alkyl ester copolymers, styrene-methacrylic acid-acrylic alkyl ester copolymers, styrene-methacrylic acid-acrylic alkyl ester copolymers, styrene-maleic acid half ester copolymers, etc., which have a weight average molecular weight in the range of 5000 to 30000. Especially preferred: are copolymers of a (meth)acrylic ester having an alkyl group having 8 to 20 carbon atoms, a (meth)acrylic ester having an alkyl group having 1 to 7 carbon atoms and (meth)acrylic acid.

The aqueous resin desirably exists in an amount ranging from 0.1 to 20% by weight, preferably 0.2 to 10% by weight on the basis of the ink composition for ink-jet recording.

The basic compound for dissolving an aqueous resin into an aqueous medium includes alkaline metal hydroxides such as NaOH, KOH; alkylamines such as butylamine, triethylamine; alkanolamines such as monoethanolamine, diethanolamine, triethanolamine; morpholine; ammonia water, etc.

Ink compositions for ink-jet recording according this invention may also include various additives such as surfactants, pigment dispersants, viscosity controllers, defoamers, etc., if desired.

Ink compositions for ink-jet recording may be prepared with the above described components by a process comprising the steps of mixing a pigment, a compound wherein ethylene oxide is added to polyglycerin, an aqueous medium, and if desired, an aqueous resin, basic compound, surfactant, pigment dispersant, viscosity controller, defoamer, etc., then dispersing the pigment by means of any of various dispersing machines such as ball mill, roll mill, sand mill, and adding and mixing the remainder of the materials.

In this invention, a desired particle size distribution may be given to the pigment by using grinding media of a small size or at a high filling ratio in the dispersing media, or prolonging the treatment period, or lowering the treatment speed, or classifying particles through a filter or centrifuge after dispersion, or other means.

This invention will now be illustrated by way of examples, but these examples should not be construed as limiting this invention. In the following examples, "parts" means "parts by weight" unless otherwise indicated.

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#### Example 8

The procedure of Example 2 was followed except that 5.0 parts of carbon black were replaced by 5.0 parts of copper phthalocyanine blue (C.I. Pigment Blue 15:3, product of Dainippon Ink and Chemicals, Inc.) to give an ink composition for ink-jet recording 8.

#### Example 9

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The procedure of Example 2 was followed except that 5.0 parts of carbon black were replaced by 5.0 parts of dimethyl quinacridone (C.I. Pigment Red 122, product of Dainippon Ink and Chemicals, Inc.) to give an ink composition for ink-jet recording 9.

#### Example 10

The procedure of Example 2 was followed except that 5.0 parts of carbon black were replaced by 5.0 parts of disazo yellow (C.I. Pigment Yellow 83, product of Hoechst AG) to give an ink composition for ink-jet recording 10.

#### Example 11

The procedure of Example 2 was followed except that 6.0 parts of diethylene glycol were replaced by 6.0 parts of a compound wherein 20 moles of ethylene oxide are added to polyglycerin (polymerization degree: 4) to give an ink composition for ink-jet recording 11.

#### Example 12

After 4.0 parts of the water-soluble resin varnish prepared in Example 2, 5.0 parts of carbon black (C.I. Pigment Black 7, product of Mitsubishi Chemical Corp.), 20.0 parts of a compound wherein 20 moles of ethylene oxide are added to polyglycerin (polymerization degree: 4) and 5.0 parts of ion exchange water were premixed for one hour, the pigment was dispersed by means of a sand mill according to a conventional method. Then 66.0 parts of ion exchange water were further added to give an ink composition for ink-jet recording 12.

# Comparative Example 1

The procedure of Example 2 was followed except that 5.7 parts of a compound wherein 20 moles of ethylene oxide are added to polyglycerin (polymerization degree: 4) were replaced by 5.7 parts of a compound wherein 3 moles of ethylene oxide are added to polyglycerin (polymerization degree: 4) to give an ink composition for ink-jet recording 13.

# Comparative Example 2

The procedure of Example 2 was followed except that 5.7 parts of a compound wherein 20 moles of ethylene oxide are added to polyglycerin (polymerization degree: 4) were replaced by 5.7 parts of a compound wherein 95 moles of ethylene oxide are added to polyglycerin (polymerization degree: 4) to give an ink composition for ink-jet recording 14.

# Comparative Example 3

The procedure of Example 1 was followed except that 5.7 parts of a compound wherein 5 moles of ethylene oxide are added to polyglycerin (polymerization degree: 4) were replaced by diethylene glycol to give an ink composition for ink-jet recording 15.

# Evaluation of Examples 1 to 12 and Comparative Examples 1 to 3

The ink compositions for ink-jet recording 1 to 15 obtained in Examples 1 to 12 and Comparative Examples 1 to 3 were subjected to an evaluation test for clogging of nozzles according to the following procedure. The results are shown in Table 1.

#### Clogging of nozzles

In a recording apparatus having on-demand type multiple heads wherein recording takes place by applying heat



# EUROPEAN SEARCH REPORT

Application Number EP 97 30 2429

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|----------|---|--|---|---|
| Category | Citation of document with inc<br>of relevant pass   |  | Relevant<br>to claim  | CLASSIFICATION OF THE APPLICATION (Int.Cl.6)                    |
| x        | February 1993   | UBISHI PENCIL CO) 26<br>ine 32; claims 1-11 *<br>line 31 *                                 | 1-3   | C09D11/00<br>C08G65/26<br>C08L71/02                             |
| Α        | EP 0 211 278 A (CANC<br>* page 9, line 9 - 1<br>* page 11, line 1 -   | <br>DN KK) 25 February 1987<br>ine 14 *<br>line 26 *                                       | 1,2   |   |
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|          |   |  |   | TECHNICAL FIELDS<br>SEARCHED (Int.CJ.6)<br>CO9D<br>CO8G<br>CO8L |
|          |   | -  |   |   |
|          | The present search report has been drawn up for all claims  |  |   |   |
|          | Place of search   | Date of completion of the search   |   | Examiner  |
|          | THE HAGUE   | 17 July 1997   | Mi  | ller, A   |
| Y:p      | CATEGORY OF CITED DOCUME<br>articularly relevant if taken alone<br>articularly relevant if combined with an<br>ocument of the same category<br>echnological background<br>on-written disclosure<br>itermediate document | E : earlier patent d<br>after the filing<br>other D : document cited<br>L : document cited | ocument, but pudate<br>in the applicati<br>for other reason | iblished on, ur<br>on<br>is                                     |